

AN IMPROVED PROCESS FOR THE PREPARATION OF BIO-DIESEL

Field of the invention:

The present invention relates to an improved process for the preparation of bio-diesel. It has enormous potential application in automobile industry as a substitute fuel for diesel.

Background of the invention:

Biodiesel has of late been recognized as an efficient fuel substitute. As reported by Anjana Srivastava and Ram Prasad (Renewable & Sustainable Energy Reviews – 4, 2000, p111-133,) renewable sources such as vegetable oils, animal fats and used cooking oils are normally used as the starting material for preparing this alternate source of fuel. There are also reports that, the engine problems due to carbonization of combustion chamber and wax deposits & engine failure.

As reported by Gerhard Vellguth (Society of Automobile Engines No. 831358, 1983), the fuel injector modifications are needed in standard diesel engines while using vegetable oil as a fuel, otherwise forms deposits on the injectors and in the cylinder head, leading to poor performance, higher emissions and reduces engine life. This limitation has to some extent been resolved by way of transesterification.

Reference may be made to Antolin et al., (Bioresource Technology 83, 2002, p111-114), who transesterified sunflower oil with methanol at a temperature in the range of 40-70 °C under constant stirring for a period of 2-6 hrs. Similar efforts have been made by different research groups to prepare biodiesel from multiple oil sources. As reported by Alcantara et al., (Biomass Bioenergy 18,p515-527,2000) several oils such as soybean, frying oil, tallow have been tried as substitutes for diesel. As reported by Widyan and Shyouch (Bioresource Technology 85, p253-256,2002), palm oil has also been tried as substitutes.

Conventionally, biodiesel is prepared from oil by reacting with alcohol using a acid/alkali/enzyme catalyst in the temperature range of 40-80 °C under constant stirring for a period of 2-6 hrs. In order to achieve higher product conversion, 1-3

moles per moles of oil in excess to stoichiometric quantity of alcohol is normally used and the unreacted alcohol is removed in the subsequent process steps. The ester obtained is separated from glycerine by suitable separation process and the ester is washed with mild acid. The product is purified further by evaporation to remove unreacted alcohol and traces of moisture. The final product is normally used in combination with regular petroleum fuels to overcome the viscosity and related problems.

The major limitation associated with all these processes is that the overall product conversion in most of the cases is limited to 60-85% only. Moreover, the temperature range limited up to 60°C results in prolonged time, which may be as high as 6 hrs and thereby enhancing the cost of the process significantly.

Another limitation associated with these processes is that the resulting product exhibits higher viscosity compared with conventional petroleum fuels, thereby necessitating it is blending with petroleum fuels for the use in diesel engines.

Objects of the invention:

The main object of the present invention is to provide an improved process for the preparation of bio-diesel which obviates the limitations as stated above.

Another object of the present invention is to provide a chemical process for biodiesel with renewable sources of energy.

Still another object of the present invention is to provide a chemical process for biodiesel oil preparation from extracted from agricultural edible and non-edible products.

Yet another object of the present invention is to provide an environmentally friendly fuel.

Still yet another object of the present invention is to provide an improved quality of biodiesel can be used with out any alteration in the diesel engine.

Accordingly the present invention provides an improved process for the preparation of bio-diesel, which comprises

- i) heating oil, characterized by specific gravity in the range of 0.85 – 0.96 and iodine value not exceeding 208, to a temperature not exceeding 120°C for not less than 2hrs followed by transesterification with 8 to 42% w/w, of alcohol of general formula R-OH, where R represents (C_nH_{2n+1}) , n being any integer between 1 and 5, by known method in presence of not more than 0.55% w/w, of a known catalyst, at a temperature higher than the boiling point of the alcohol but not exceeding 215°C for a period of not less than 30 minutes under continuous turbulent condition to get mixture of ester and glycerol,
- ii) subjecting the mixture, as formed in step(i) to separation of the esterified oil by known method for a period of not less than 4 hrs followed by conventional purification for a period of not less than 8 hrs. and repeating the process of separation as well as purification in succession for not less than three times to get biodiesel.

In an embodiment of the present invention the oil used may be selected from ricebran oil, cottonseed oil, soybean oil, sunflower oil, castor oil, coconut oil.

In another embodiment of the present invention the alcohol used may be selected from methanol, ethanol, n-propanol, n-butanol, n-pentanol

In yet another embodiment of the present invention the catalyst used may be selected from sodium hydroxide, potassium hydroxide.

In still another embodiment of the present invention, the known method of separation used may be such as decanting, centrifuging, gravity separation, settling.

In yet another embodiment of the present invention the conventional method of purification used may be selected from bubble washing involving bubble size of 1-3mm, micro filtration with not less than 5micron filter, centrifuging, either alone or in any combination.

In still another embodiment of the present invention, the Reynolds number (N_{Re}) used for maintaining turbulence may be adjusted at not less than 4000 irrespective of the type of reactor.

The process of the present invention is described below in detail.

Oil having specific gravity in the range of 0.85 – 0.96 and iodine value not exceeding 208 is heated to a temperature not exceeding 120°C for not less than 2hrs and is transesterified using 8 to 42% w/w, of alcohol of general formula R-OH, where R represents (C_nH_{2n+1}) , n being any integer between 1 and 5, by known method in presence of not more than 0.5% w/w, of a known catalyst, at a temperature higher than the boiling point of the alcohol but not exceeding 215°C for not less than 30 minutes under continuous turbulent condition at rpm in the range of 100-150 to get a mixture of ester and glycerol. The Reynolds number (N_{Re}) is maintained at not less than 4000 irrespective of the type of the reactor.

The mixture of ester and glycerol is subjected to separation by known method for a period of not less than 4 hrs and the top layer ester is purified by conventional method for a period of not less than 8hrs. The process of separation as well as purification is repeated for not less than three times in succession to get biodiesel.

The inventive step of the present invention lies not only in selecting the temperature of transesterification at higher than the boiling point of the alcohol while not exceeding 215°C, but also in maintaining turbulence monitored by adjusting the Reynolds number (N_{Re}) at not less than 4000 irrespective of the type of the reactor, to ensure about 97% conversion of the oil into ester within a period of as low as 30 minutes, thereby enhancing the formation of fuel properties in the resulting product called biodiesel.

The following examples are given by way of illustration only and therefore should not be construed to limit the scope of the present invention.

Example 1

100 ml of rice bran oil having a moisture content of 3% was heated at 120° C for a period of 2 hrs. Later the moisture content of the oil was found to be 0.5%.

This oil was taken in the specially modified batch Continuous Stirred Tank Reactor (CSTR) with provision for alcohol recycle/recovery system, condenser, thermometer and feeding funnel. 20ml of methanol was taken in a beaker and 0.5gm sodium hydroxide was added to it under continuous stirring. The resulting solution was then added to the reactor rapidly. The reactor system was maintained at turbulent condition by stirring at 100 rpm in order to maintaining the Reynolds number (N_{Re}) at the minimum of 4000. The reaction was continued for 30 minutes. The excess methanol of 4 ml used for above reaction was later is recovered.

The resulting solution was taken in separating funnel, and two layers were found to form. The mixture was allowed to settle for 4 hrs and the top layer was taken for further processing.

This was then subjected to bubble washing by aeration with 15ml of distilled water for a period of 8 hrs and the resulting material was allowed to settle for 8hrs. It was taken for micro filtration to remove the micro particles present in the product. The bubble washing, settling and filtration operations were repeated for two more times to attain improved fuel properties. The resulting biodiesel was stored.

97% of rice bran oil was estimated to has been converted into biodiesel, which was found to meet the specifications of conventional petroleum fuel. The biodiesel was used for running a test engines. The emission properties of this biodiesel were found to be better than of the conventional fuels.

Example 2

100 ml of rice bran oil having a moisture content of 3% was heated at 120° C for a period of 2 hrs. Later the moisture content of the oil was found to be 0.5%.

This oil was taken in the specially modified batch Continuous Stirred Tank Reactor (CSTR) with provision for alcohol recycle/recovery system, condenser, thermometer and feeding funnel. 32ml of propanol was taken in a beaker and 0.5gm sodium hydroxide was added to it under continuous stirring. The resulting solution was then

added to the reactor rapidly. The reactor system maintained at turbulent condition by stirring at 100-rpm in order to maintaining the Reynolds number (N_{Re}) at the minimum of 4000. The reaction was continued for 30 minutes. The excess methanol of 7 ml used for above reaction was later is recovered by the special recovery system. The resulting solution was taken in separating funnel, and two layers were found to form. The mixture was allowed to settle for 4 hrs and the top layer was taken for further processing.

This was then subjected to bubble washing by aeration with 25ml of distilled water for a period of 8 hrs and the resulting material was allowed to settle for 8hrs. It was taken for micro filtration to remove the micro particles present in the product. The bubble washing, settling and filtration operations were repeated for two more times to attain improved fuel properties. The resulting biodiesel was stored.

95% of rice bran oil was estimated to has been converted into biodiesel, which was found to meet the specifications of conventional petroleum fuel. The biodiesel was used for running a test engines. The emission properties of this biodiesel were found to be better than of the conventional fuels.

Example 3

100 ml of sunflower oil having a moisture content of 1.5% was heated at 120° C for a period of 2 hrs. Later the moisture content of the oil was found to be 0.5%.

This oil was taken in the specially modified batch Continuous Stirred Tank Reactor (CSTR) with provision for alcohol recycle/recovery system, condenser, thermometer and feeding funnel. 40 ml of butanol was taken in a beaker and 0.5gm sodium hydroxide was added to it under continuous stirring. The resulting solution was then added to the reactor rapidly. The reactor system maintained at turbulent condition by stirring at 100-rpm in order to maintaining the Reynolds number (N_{Re}) at the minimum of 4000. The reaction was continued for 30 minutes. The excess butanol of 8.3 ml used for above reaction was later is recovered by the special recovery system.

The resulting solution was taken in separating funnel, and two layers were found to form. The mixture was allowed to settle for 4 hrs and the top layer was taken for further processing.

This was then subjected to bubble washing by aeration with 15ml of distilled water for a period of 8 hrs and the resulting material was allowed to settle for 8hrs. It was taken for micro filtration to remove the micro particles present in the product. The bubble washing, settling and filtration operations were repeated for two more times to attain improved fuel properties. The resulting biodiesel was stored.

98.0% of sunflower oil was estimated to have been converted into biodiesel, which was found to meet the specifications of conventional petroleum fuel. The biodiesel was used for running a test engines. The emission properties of this biodiesel were found to be better than of the conventional fuels.

Example 4

200 ml of coconut oil having a moisture content of 2% was heated at 120° C for a period of 2 hrs. Later the moisture content of the oil was found to be 0.5%.

This oil was taken in the specially modified batch Continuous Stirred Tank Reactor (CSTR) with provision for alcohol recycle/recovery system, condenser, thermometer and feeding funnel. 47 ml of methanol was taken in a beaker and 1gm sodium hydroxide was added to it under continuous stirring. The resulting solution was then added to the reactor rapidly. The reactor system maintained at turbulent condition by stirring at 100-rpm in order to maintaining the Reynolds number (N_{Re}) at the minimum of 4000. The reaction was continued for 60 minutes. The excess methanol of 10 ml used for above reaction was later is recovered by the special recovery system.

The resulting solution was taken in separating funnel, and two layers were found to form. The mixture was allowed to settle for 8 hrs and the top layer was taken for further processing.

This was then subjected to bubble washing by aeration with 15ml of distilled water for a period of 8 hrs and the resulting material was allowed to settle for 8hrs. It was taken for micro filtration to remove the micro particles present in the product. The bubble washing, settling and filtration operations were repeated for two more times to attain improved fuel properties. The resulting biodiesel was stored.

98.0% of coconut oil was estimated to have been converted into biodiesel, which was found to meet the specifications of conventional petroleum fuel. The biodiesel was used for running a test engines. The emission properties of this biodiesel were found to be better than of the conventional fuels.

Example 5

100 ml of coconut oil having a moisture content of 2% was heated at 120° C for a period of 2 hrs. Later the moisture content of the oil was found to be 0.5%.

This oil was taken in the specially modified batch Continuous Stirred Tank Reactor (CSTR) with provision for alcohol recycle/recovery system, condenser, thermometer and feeding funnel. 35 ml of ethanol was taken in a beaker and 0.5gm sodium hydroxide was added to it under continuous stirring. The resulting solution was then added to the reactor rapidly. The reactor system maintained at turbulent condition by stirring at 100-rpm in order to maintaining the Reynolds number (N_{Re}) at the minimum of 4000. The reaction was continued for 45 minutes. The excess ethanol of 8 ml used for above reaction was later is recovered by the special recovery system.

The resulting solution was taken in separating funnel, and two layers were found to form. The mixture was allowed to settle for 8 hrs and the top layer was taken for further processing.

This was then subjected to bubble washing by aeration with 15ml of distilled water for a period of 8 hrs and the resulting material was allowed to settle for 8hrs. It was taken for micro filtration to remove the micro particles present in the product. The bubble washing, settling and filtration operations were repeated for two more times to attain improved fuel properties. The resulting biodiesel was stored.

97.0% of coconut oil was estimated to have been converted into biodiesel, which was found to meet the specifications of conventional petroleum fuel. The biodiesel was used for running a test engines. The emission properties of this biodiesel were found to be better than of the conventional fuels.

Example 6

100 ml of sunflower oil having a moisture content of 1.5% was heated at 120° C for a period of 2 hrs. Later the moisture content of the oil was found to be 0.5%.

This oil was taken in the specially modified batch Continuous Stirred Tank Reactor (CSTR) with provision for alcohol recycle/recovery system, condenser, thermometer and feeding funnel. 20 ml of methanol was taken in a beaker and 0.5gm sodium hydroxide was added to it under continuous stirring. The resulting solution was then added to the reactor rapidly. The reactor system maintained at turbulent condition by stirring at 100-rpm in order to maintaining the Reynolds number (N_{Re}) at the minimum of 4000. The reaction was continued for 30 minutes. The excess methanol of 4 ml used for above reaction was later is recovered by the special recovery system. The resulting solution was taken in separating funnel, and two layers were found to form. The mixture was allowed to settle for 4 hrs and the top layer was taken for further processing.

This was then subjected to bubble washing by aeration with 15ml of distilled water for a period of 8 hrs and the resulting material was allowed to settle for 8hrs. It was taken for micro filtration to remove the micro particles present in the product. The bubble washing, settling and filtration operations were repeated for two more times to attain improved fuel properties. The resulting biodiesel was stored.

98.0% of sunflower oil was estimated to have been converted into biodiesel, which was found to meet the specifications of conventional petroleum fuel. The biodiesel was used for running a test engines. The emission properties of this biodiesel were found to be better than of the conventional fuels.

Example 7

100 ml of sunflower oil having a moisture content of 1.5% was heated at 120° C for a period of 2 hrs. Later the moisture content of the oil was found to be 0.5%.

This oil was taken in the specially modified batch Continuous Stirred Tank Reactor (CSTR) with provision for alcohol recycle/recovery system, condenser, thermometer and feeding funnel. 25 ml of ethanol was taken in a beaker and 0.5gm sodium hydroxide was added to it under continuous stirring. The resulting solution was then added to the reactor rapidly. The reactor system maintained at turbulent condition by stirring at 100-rpm in order to maintaining the Reynolds number (N_{Re}) at the minimum of 4000. The reaction was continued for 30 minutes. The excess ethanol of 8ml used for above reaction was later is recovered by the special recovery system.

The resulting solution was taken in separating funnel, and two layers were found to form. The mixture was allowed to settle for 4 hrs and the top layer was taken for further processing.

This was then subjected to bubble washing by aeration with 15ml of distilled water for a period of 8 hrs and the resulting material was allowed to settle for 8hrs. It was taken for micro filtration to remove the micro particles present in the product. The bubble washing, settling and filtration operations were repeated for two more times to attain improved fuel properties. The resulting biodiesel was stored.

98.0% of sunflower oil was estimated to have been converted into biodiesel, which was found to meet the specifications of conventional petroleum fuel. The biodiesel was used for running a test engines. The emission properties of this biodiesel were found to be better than of the conventional fuels.

Emission Analysis of Diesel, Biodiesel and Various Blends

Load KW	Sample	Time for 10cc(sec)	CO (%vol)	CO₂ (%vol)	HC (ppm)	O₂ (%VOL)	NOx (ppm)	Noise (db)	T_{exh} (°c)
0	Diesel	65	0.08	2.1	28	17.53	180	145	140
	Biodiesel	65	0.04	2.55	10	17.10	111	116	182
	BS1	66	0.02	2.31	0	17.30	154	145	153
	BS2	71	0.02	2.14	0	17.50	96	112	154
	BS3	69	0.03	2.13	0	17.36	125	113	145
	BS4	69	0.03	2.42	5	17.28	113	120	170
	BS5	78	0.04	2.09	0	17.47	84	115	169
4	Diesel	49	0.12	3.5	43	15.62	397	145	210
	Biodiesel	45	0.04	3.95	20	15.27	118	119	202
	BS1	51	0.03	3.61	0	15.70	369	120	190
	BS2	49	0.03	3.49	27.5	15.57	277	112	196
	BS3	48	0.03	3.84	20	14.94	300	115	180
	BS4	49	0.04	3.90	17.5	16.39	283	129	245
	BS5	48	0.045	4.02	2.5	14.99	300	116	242
7	Diesel	42	0.13	4.3	63	14.68	582	146	243
	Biodiesel	36	0.03	5.06	10	13.53	525	121	277
	BS1	46	0.04	4.11	35	14.73	473	117	210
	BS2	39	0.04	4.87	12.5	13.56	502	114	225
	BS3	38	0.05	5.44	10	12.67	479	116	243
	BS4	38	0.05	5.20	10	13.18	496	126	285
	BS5	38	0.06	5.46	32.5	12.85	451	119	315
11	Diesel	32	0.2	6.3	85	11.2	689	159	287
	Biodiesel	30	0.05	6.74	20	10.99	727	123	329
	BS1	32	0.06	6.79	37.5	10.53	800	119	250
	BS2	29	0.06	6.91	15	10.43	728	118	240
	BS3	30	0.10	7.05	15	10.15	608	119	285
	BS4	30	0.10	7.35	45	9.83	605	126	296
	BS5	30	0.11	7.01	30	10.36	616	121	362
14	Diesel	27	0.34	7.7	89	9.12	942	169	294
	Biodiesel	25	0.09	8.30	35	8.74	904	124	411
	BS1	27	0.07	7.58	35	9.24	977	120	266
	BS2	26	0.18	8.04	47.5	8.54	858	119	363
	BS3	23	0.27	9.03	52.5	6.86	782	122	342
	BS4	27	0.14	8.10	45	8.60	782	127	395
	BS5	24	0.24	8.30	45	8.22	660	123	380

Note: BS- Blended with Diesel

BS1- B20, BS2- B80, BS3-B50, BS4-B40, BS5- B60

OIL SPECIFICATION

Specific gravity	: 0.916 – 0.912
Refractive Index	: 1.470 – 1.473
Iodine value	: 99 - 108
Saponification value	: 181 - 189
Acid value	: 4 - 120
Titer	: 24 - 28°C
Unsaponifiable matter	: 3.5 %
Tocopherols average	: 400 mg/kg of oil

Fuel properties

Property	DIESEL	Biodiesel (RBOE)
Density (gm/cc)	0.82	0.865
Viscosity (Cst)	2.4	3.46
Heat Of Combustion (MJ/Kg)	42.57	45.09
Flash Point (°C)	74	182
Fire Point (°C)	87	194
Copper strip Corrosion @ 100 (°C)	No.3	< No.1

Engine Efficiency

Load (kW)	Specific Fuel Consumption (kWh)		Break Thermal Efficiency (%)		Mechanical Efficiency (%)		Indicative Thermal Efficiency (%)	
	Diesel	Biodiesel	Diesel	Biodiesel	Diesel	Biodiesel	Diesel	Biodiesel
0	∞	∞	0	0	0	0	20.65	30.22
4	0.556	0.611	15.07	14.01	47.41	37.54	31.77	37.33
7	0.378	0.419	22.17	20.08	62.22	51.27	36.22	40.46
11	0.314	0.333	26.67	25.69	71.26	62.31	37.42	41.23
14	0.292	0.328	28.65	26.07	75.94	67.78	37.73	38.45

A comparative study of the Complete specification relating to P03ce04 (an improved process for the preparation of bio-diesel) and the US patent No. 6,015,440 apparently reveals the following differences.

Sl.No	US patent No. 6,015,440	Bio-diesel Process – Ref No. P03ce04/CLRI
1.	Temperature range of the reaction 70-80° C	More than the boiling point of the alcohol but less than 215° C
2.	Pressure at 20 psig	Atmospheric pressure
3.	Separation alkali using ion	Separation of alkali using water

	exchange column	
4.	Top layer approximately 80%	More than 80%
5.	Un-reacted methanol removal by an addition process step of flash recovery system (in a separate reactor)	Un-reacted methanol has separated immediately after the reaction by a specially modified provision built within on within the reactor
6.	Fixed bed/Plug flow reactor	Batch reactor
7.	Multiple reactor	Single reactor consists of special provision for excess alcohol recovery
8.	Continuous process	Batch process
9.	Increased final product volume due to blending of higher fatty acid ester with glyceryl ether.	The final product contains only higher fatty acid esters.
10.	Reaction with isobutylene	No such reaction
11.	Oxidative process	Base catalysed transesterification
12.	Product is Mixture of Bio-diesel and Ester glycerol	The final product contains higher fatty acid esters.
13.	Transesterifying at least a portion only	Almost all portion.
14.	This end product of this process is a mixture of ester and the etherified glycerol, which is converted into bio-diesel by blending.	The end product is bio-diesel, no mixing with glycerol. In fact glycerol is obtained as by-product
15.	Only by mixing the etherified glycerol to the esterified oil may gives the viscosity reduction.	This is a bio-diesel process, without mixing the glycerol, with all required bio-diesel properties and emission norms similar to the normal diesel fuel.
16.	Strong acid catalyst process	Alkali/ base catalyst process
17.	Approximately 80% of the bio-diesel is in pure form	More than 95% in pure form
18.	Effect of mixing of etherified crude glycerol's effect in the engine is not defined, shown only the viscosity reduction	No engine difficulties. No need of any change in the engine needed, no engine block etc.
19.	Low waste process, not separating the 20% crude glycerol formed.	More than 95% conversion. Glycerol formed as a by-product can be used in other industries.
20.	Formation of 20% glycerol, for economical purpose, after reacting with isobutylene mixing with the bio-diesel	Glycerol formed as a by-product can be used in other industries.
21.	After mixing the crude glycerol only, the product gives properties closely resembling to have of diesel fuel	The final product after the reaction is similar to diesel fuel

In our opinion, the inventive step of the present invention vis-à-vis the aforesaid US Patent document, however, essentially lies in conducting the reaction at a temperature higher than the boiling point of the alcohol used, besides maintaining the turbulence ($N_{Re} = 4000$ or more), that is applicable irrespective of the type of the reactor used, to enhance the fuel properties of the resulting product. This step ensures that no blending, as described in the US Patent document.

Following are some of the advantages of the present invention :

1. The high temperature with turbulent condition (Reynolds number more than 4000), reduces the reaction time significantly.
2. The special provision in the reactor enables the effective recovery of excess alcohol added for the reaction.
3. Bubble washing and microfiltration achieved the high quality of the biodiesel.
4. The product is based on renewable source.
5. The product can be used as substitute fuel for diesel engines without any major modification of engines.
6. The final product is a substitute fuel for diesel without blending with other conventional petroleum fuels.
7. The products fuel properties and the engine efficiency are comparable with normal diesel engine fuels.
8. The emission characteristics are like those of normal fuels.